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**Bifunctional catalysts for CO<sub>2</sub> reduction**

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## A. Specific Aims

1. Synthesize mono- and dinucleating ligands and their derivatives; the latter featuring two chemically/electronically distinct binding sites to support homo- and heterobimetallic complexes for CO<sub>2</sub> fixation. Modification of the original design led us to also pursue the formation of cluster based catalyst platforms. Details for the construction of these materials, as they deviate from the salen/salan platforms will be described below.
2. Probe the efficacy of the resulting complexes to activate CO<sub>2</sub>, targeting C–O bond heterolysis. This specific activity will be probed as a function of catalyst composition using different combinations of transition metals, alkali/alkaline metals and secondary hydrogen-bonding networks.
3. Develop the catalytic competency of the resulting systems for efficient electrochemical reduction of CO<sub>2</sub> into CO and water. Determine CO<sub>2</sub> reduction efficacy and product distribution as a function of catalyst composition (ligand, metal ions), electrolyte, acid and CO<sub>2</sub> pressure.
4. Examine reaction chemistry of electrophilic complexes to activate CO towards reductive CO-coupling processes and develop stoichiometric reaction into viable catalytic processes.

## B. Studies and Results

We have developed dinucleating ligand platforms to present both nucleophilic and electrophilic functionalities for the cooperative activation of carbon dioxide. Our efforts to achieve this center on the following objectives: (1) design and synthesis of salen-based ligands for catalyst stabilization; (2) investigate substrate activation under stoichiometric and catalytic conditions; and (3) optimization of carbon dioxide reduction catalysis.

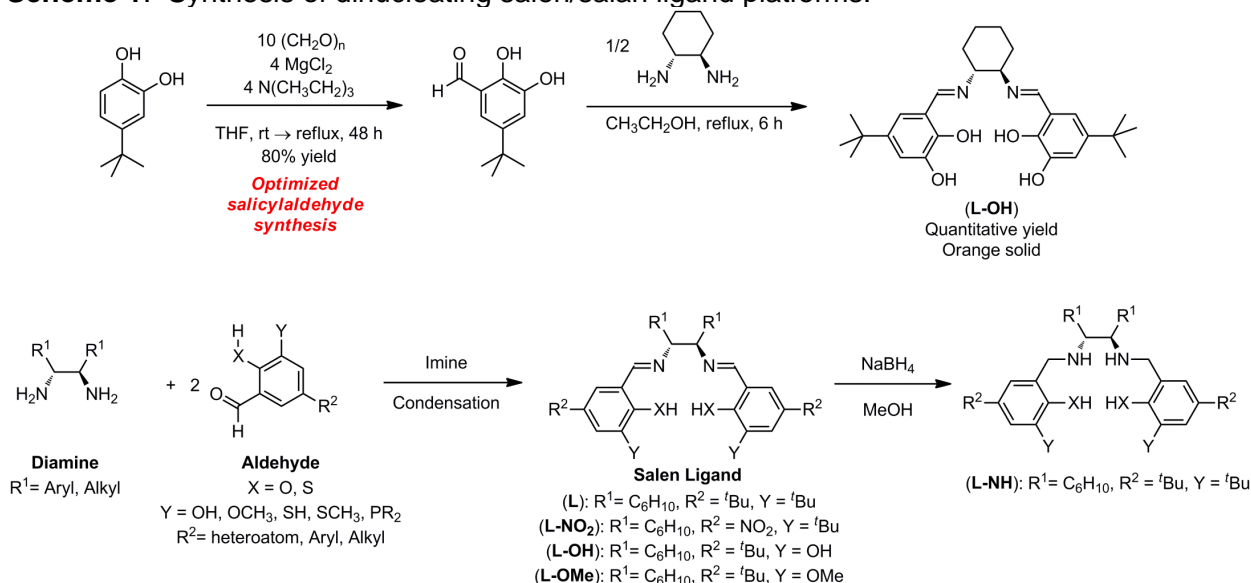
(SA 1 – *Catalyst candidate synthesis*) As outlined in the original proposal, ligand platforms have been synthesized to stabilize both a low-valent, nucleophilic metal center (focus on Fe and Co ions), in addition to electrophilic metal agents to stabilize charge-buildup on the CO<sub>2</sub> substrate under reducing conditions. The primary coordination sphere is comprised by the salen (see Scheme 1) platform wherein both imine functionalities have been preserved or reduced to the parent amine functionalities. No permutations on the phenoxide unit have been explored (e.g., exchange of the O-based donor for softer heteroatom functionalities). The diimine/diamine backbone has been varied to provide greater crystallinity (e.g. *ortho*-phenylenediamine), although this had a negative impact on reduction potentials for the primary nucleophile (Co<sup>II/I</sup> reduction was pushed to -2.2 V vs. ferrocene couple, suggesting significantly reduced nucleophile character).

Commercially available salicylaldehydes featuring phosphine (PPh<sub>2</sub>) and amine (NMe<sub>2</sub>) functional groups were synthesized to create electron-rich secondary ion binding pockets. To encapsulate an alkali metal in the secondary coordination sphere, alkylation of the catechol-based salicylaldehyde unit with 1,5-ditosyldiethylether was achieved in moderate yield in the presence of base (K<sub>2</sub>CO<sub>3</sub>). Hybrid salen/dipyrromethene platforms have been prepared from aldehyde condensation with the 3,3'-dipyrrolide(*salen*), followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to afford the conjugated salen/dipyrin ligand platform.

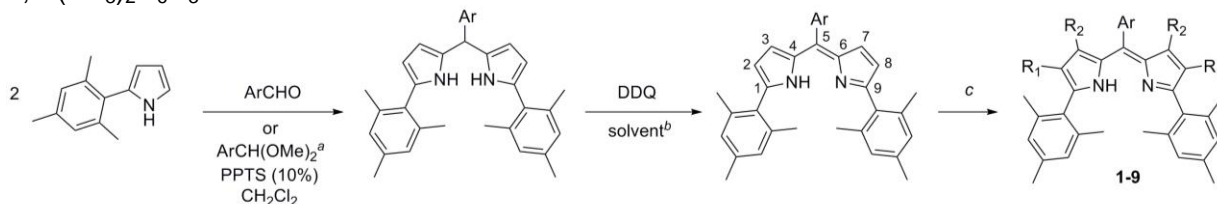
One of the significant deficiencies of the as-described salen/salan ligand platforms (see results discussion in SA 2 – *Dinucleating ligand platforms* below) was the inability to tune the redox potential of the primary nucleophile (salen/salan-bound transition metal ion). Reactivity with carbon dioxide was limited to outer-sphere electron transfer (necessary oxidation potentials for catalysis > -2.1 V vs. [Cp<sub>2</sub>Fe]<sup>+0</sup>). Thus, we pursued two alternative ligand platforms to seek transition metal complexes that would feature inner-sphere reduction chemistry with CO<sub>2</sub> and promote the desired multi-electron reduction pathway of activation. The first ligand platform is

dipyrinato-based (or semi-porphyrin). The ligand is comprised of two conjugated pyrrolides, that form one aromatic platform upon oxidation to the dipyrin. These ligands have been synthesized as described in the literature.<sup>1</sup> The results of the electronic perturbation of these complexes will be described below.

**Scheme 1.** Synthesis of dinucleating salen/salan ligand platforms.

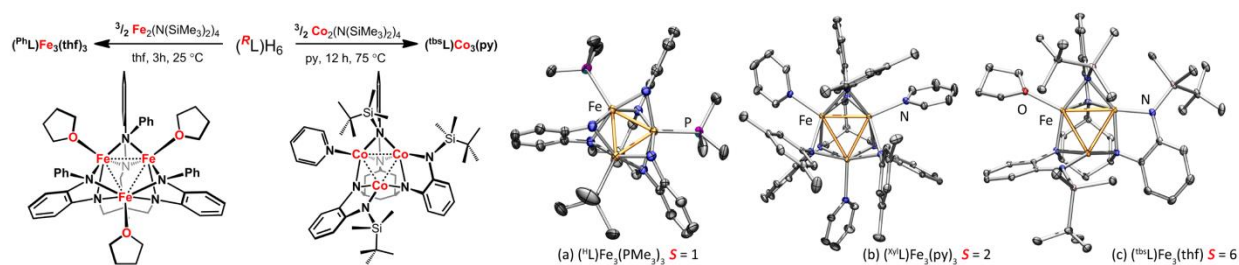


**Scheme 2.** Synthesis of modified dipyrin ligand platforms. R<sub>1-4</sub> = H, Cl, Br, I; Ar = Mes, C<sub>6</sub>F<sub>5</sub>, 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.



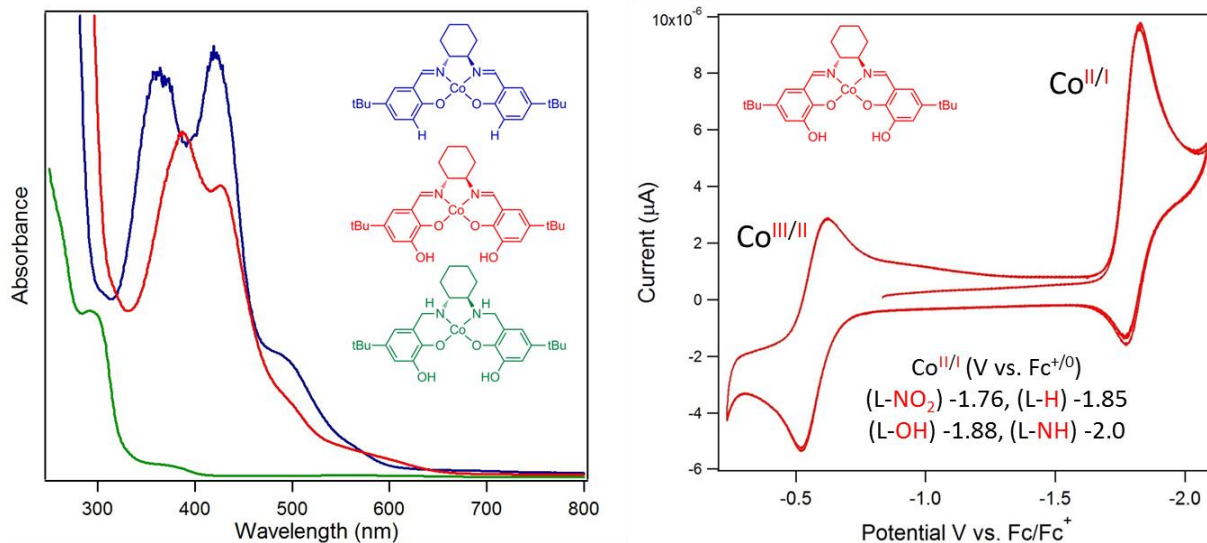
<sup>a</sup> For Ar = mesityl, acetal used; Ar = fluoroaryl, aldehyde used. <sup>b</sup> Solvent = hexanes, acetone, or CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Chlorination: 6.0 equivalents N-chlorosuccinimide, tetrahydrofuran, 70°C, 48h; bromination: N-bromosuccinimide, tetrahydrofuran, room temperature, 1-16 hr; iodination: excess I<sub>2</sub> and excess KOH, dimethylformamide, 70°C, 48h.

The second ligand platform targets cluster reaction sites. We envisioned the inclusion of multiple redox-active centers in the same reaction site would enable multi-electron reduction of the target CO<sub>2</sub> and CO substrates. Towards this end, we have synthesized both tri- and hexaanionic ligands (see Scheme 1 for representative examples) featuring triamine skeletons based on *cis,cis*-1,3,5-triaminocyclohexane. The triamine scaffolds are derivatized to feature three *o*-phenylenediamine substituents that present three binding sites to stabilize a divalent metal ion.<sup>2</sup> The simplest of these ligand types, MeC(CH<sub>2</sub>NHPh-*o*-NH<sub>2</sub>)<sub>3</sub> ((<sup>H</sup>L)H<sub>6</sub>), was shown to stabilize trinuclear manganese,<sup>3,4</sup> iron,<sup>2</sup> and cobalt<sup>4</sup> complexes. Functionalization of the peripheral anilide group permits steric tuning of the local coordination environments within the cluster, thus changing the overall molecular electronic structure.<sup>5,6</sup> As detailed in previously published work, metal installation into these polyamine based-ligands typically involves a transamination reaction with metal-amide or organometallic starting materials (e.g., M<sub>2</sub>(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>4</sub>, M<sub>n</sub>(mes)<sub>n+2</sub>), see Figure 1).



**Figure 1.** Complex synthesis and structures of (<sup>H</sup>L)Fe<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> (a), (<sup>xy</sup>L)Fe<sub>3</sub>(py)<sub>3</sub> (b), and (<sup>ts</sup>L)Fe<sub>3</sub>(thf) (c).

(SA 2 – *Dinucleating ligand platforms*) With several ligand variants in hand, we have explored the impact on the primary nucleophile redox potentials (where CO<sub>2</sub> kinetically binds and is activated). Without significant perturbations to the salen/salan platform, we have found little effect from the secondary coordination sphere units on the redox potential of divalent iron or cobalt. The mode of action proposed was primary reduction of the primary ion (e.g., Co<sup>II</sup> + e<sup>-</sup> → Co<sup>I</sup>) which could undergo a two-electron oxidative addition of CO<sub>2</sub>. For iron-substituted salen ligands, only and Fe<sup>II/III</sup> reduction is observed at -0.53 V with only ligand-based reductions at lower potentials. Examination of the Co-substituted ligand platforms reveal an accessible Co<sup>II/I</sup> reduction within the solvent window, where the reduction potential varies as a function of ligand periphery: Co<sup>II/I</sup> (V vs. [Cp<sub>2</sub>Fe]<sup>+0</sup>) L-NO<sub>2</sub> -1.76, L-H -1.85, L-OH -1.88, L-NH -2.0. While some degree of tunability is apparent from the data, the operative Co<sup>II/I</sup> reduction remains near the potential for free electron addition to CO<sub>2</sub> (-2.1 V versus [Cp<sub>2</sub>Fe]<sup>+0</sup>), suggesting little enhancement from the metal ion catalyst to act as a cathode.

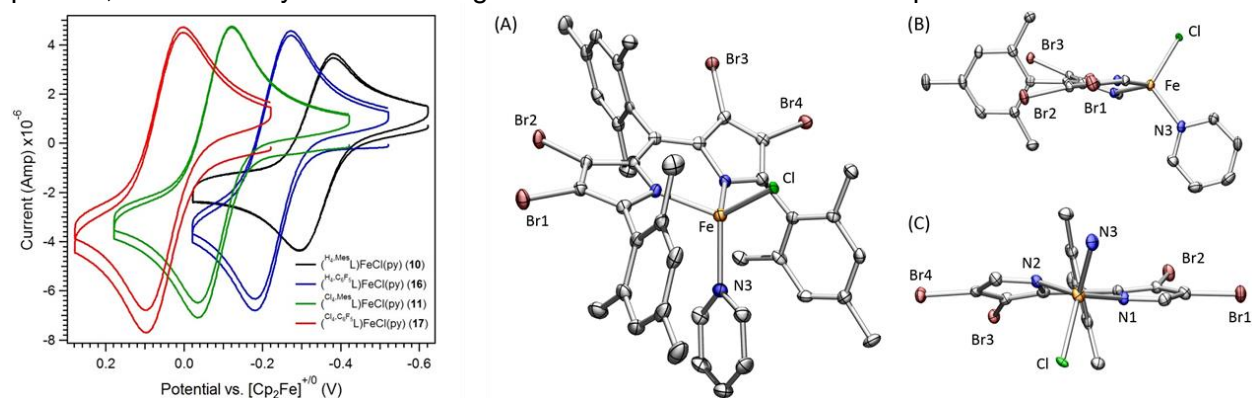


**Figure 2.** (a) UV-vis spectra for (blue) (L)Co ( $\lambda_{\text{max}}$  (nm): 359, 419, 499), (red) (L-OH)Co ( $\lambda_{\text{max}}$  (nm): 387, 426, 499), (green) (L-NH)Co ( $\lambda_{\text{max}}$  (nm): 256, 300, 390) in THF; (b) cyclic voltammograms of 1.0 mM solutions in DMF (0.1M NaClO<sub>4</sub>) of (L-OH)Co referenced to Fc/Fc<sup>+</sup> (scan rate = 50mV/min, working electrode: glassy C, counter: Pt wire, reference: Ag wire).

We have also investigated mononuclear systems featuring primary amines in the ligand secondary coordination sphere to probe for enhanced CO<sub>2</sub> uptake. The amine residues were proposed to provide a H-bonding acceptor network to stabilize CO<sub>2</sub><sup>-</sup> anion binding and facilitate

proton transfer during turnover. The efficacy of this approach was determined by forming long-lived CO<sub>2</sub>-adducts (as judged by CO<sub>2</sub> binding via IR analysis). However, addition of the amines did not aid in lowering of the primary nucleophile reduction potentials. In the absence of CO<sub>2</sub>, the addition of amines into the secondary coordination sphere had a negative impact on the Co<sup>III/I</sup> reduction potential, making the overall impact of this ligand permutation unclear.

(SA 2 – *Dipyrin platforms*) Unlike the salen/salan ligand variants, the easily-modified dipyrins permitted a variety of electronic alterations to the platform to be made and the electrochemical impact on the bound transition metal investigated. Systematic electronic variations were introduced into the monoanionic dipyrin ligand scaffold via halogenation of the pyrrolic  $\beta$ -positions and/or use of fluorinated aryl substituents in the ligand bridgehead position yielding ligands of the type ( $\beta^{Ar}L$ )H.<sup>7</sup> The electronic perturbations were probed using standard electronic absorption and electrochemical techniques on the different ligand variations and their divalent iron complexes. The electrochemical and spectroscopic behavior of the iron-bound complexes varies significantly across the series; most notably the redox potential of the fully-reversible Fe<sup>III/II</sup> couple spans more than 400 mV as electron-withdrawing substituents are appended to the dipyrromethene platform (Figure 3 left panel). While the direct correlation to inclusion of electron-withdrawing substituents to reduction in metal reduction potential was attractive, an unintended consequence of the ligand alterations was the geometric perturbation of the dipyrin itself. Tetrahalogenation of the  $\beta$ -positions of *meso*-mesityl dipyrinato iron complexes induces a deplanarization of the conjugated dipyrin core, resulting in ruffled structures that were characterized by X-ray crystallography (Figure 3 right panel). The structural distortions are caused by steric interactions between the *o*-methyl substituents of the *meso*-mesityl unit and the halogens in the C3- and C7-positions of the dipyrin. These structural distortions result in the observed decreased stability of the halogenated dipyrinato iron complexes. The reduced stability was marked by complex deterioration in both solid and liquid phases, evidenced by marked changes in the reconstituted <sup>1</sup>H NMR spectra.



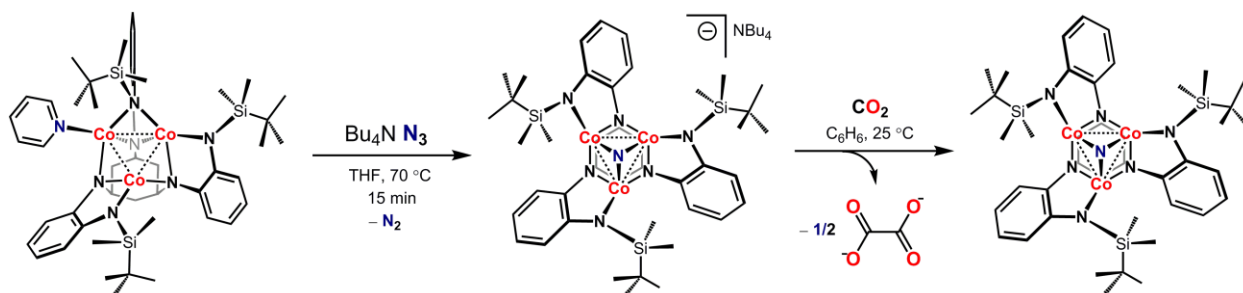
**Figure 3.** (Left panel) Fe<sup>III/II</sup> couples of representative complexes. Cyclic voltammograms obtained in THF with 0.3 M (<sup>n</sup>Bu<sub>4</sub>N)(PF<sub>6</sub>) as supporting electrolyte with a scan rate of 100 mV/sec. (Right panel) (A) Solid-state molecular structure of (Br<sub>4</sub>,MesL)FeCl(py) with side view (B) and front views (C) to illustrate dipyrin distortion.

The dipyrin-iron complexes were investigated for their reactivity with CO to elucidate CO-reductive coupling reactivity akin to that observed on a related tris-pyrrolide ligand framework (*vide infra*).<sup>8</sup> The Co-analogues were synthesized to investigate the ability to access the Co<sup>II/I</sup> reduction under milder reduction potentials than exhibited by the salen/salan Co systems. In the absence of a strongly donating co-ligand (e.g. PMe<sub>3</sub>), reduction of both the iron and cobalt divalent precursors was not observed until beyond the dipyrin ligand-based reduction at -2 V. Thus, accessing the monovalent complexes required very strong reductants



(e.g. K or Na metal) to support metal reduction. Thus, these platforms were not attractive from an electroreduction perspective and not pursued further in this work.

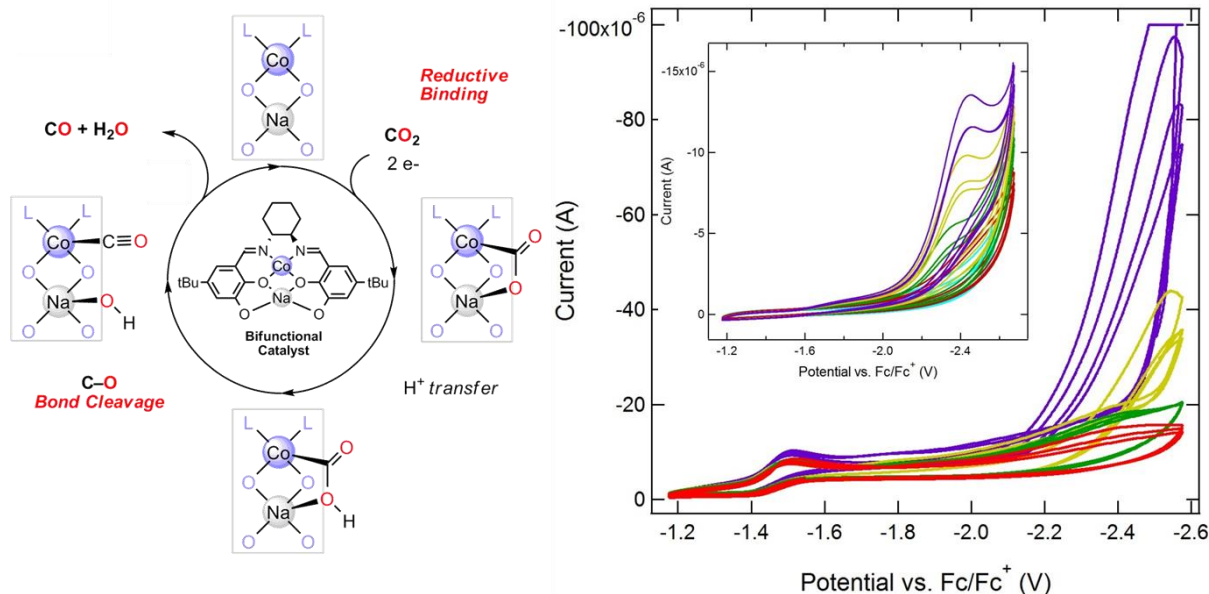
(SA 2 – *Cluster reaction site*) Given the inability to achieve the desired reduction potentials to achieve Co<sup>I</sup> within the salen/salan or dipyrin frameworks, we pursued the synthesis of an active Co-based cluster to investigate CO<sub>2</sub> reduction. We were able to observe small-anion reduction with the (<sup>t</sup>bsL)Fe<sub>3</sub>(thf) wherein inorganic azide could be reduced to the corresponding anionic nitride product [(<sup>t</sup>bsL)Fe<sub>3</sub>(μ<sup>3</sup>-N)]NBu<sub>4</sub>.<sup>9</sup> Furthermore, the resulting nitride product is cathodically shifted from the all-ferrous starting material, a result of anionic nitride ligand and the metals coming into closer proximity.<sup>10</sup> We hypothesized that moving from iron to cobalt would increase the basicity of the trinuclear core and make atom and group-transfer processes even more facile. To probe this we investigated the reactivity of (<sup>t</sup>bsL)Co<sub>3</sub>(py). Reaction of (<sup>t</sup>bsL)Co<sub>3</sub>(py) with Bu<sub>4</sub>N[N<sub>3</sub>] yields the azide adduct Bu<sub>4</sub>N[(<sup>t</sup>bsL)Co<sub>3</sub>(μ<sup>3</sup>-N<sub>3</sub>)] which features a C<sub>3</sub>-symmetric, paramagnetically shifted <sup>1</sup>H NMR and a prominent azide stretch in the IR at ν<sub>N<sub>3</sub></sub> = 2047cm<sup>-1</sup>. This material is stable indefinitely at room temperature but upon heating to 70 °C for 15 min produces a paramagnetically shifted <sup>1</sup>H NMR spectrum with consumption of the azide as determined by disappearance of ν<sub>N<sub>3</sub></sub> in the IR. The hexane soluble material was crystallized at -35 °C permitting characterization by X-ray diffraction to identify [(<sup>t</sup>bsL)Co<sub>3</sub>(μ<sup>3</sup>-N)]NBu<sub>4</sub> as the product. The bonding metrics of the nitride product are contracted compared to those reported for the iron analogue,<sup>9</sup> where the highly pyramidalized nitride ligand resides 1.159(2) Å above the mean tricobalt plane with short Co–N (1.821(2) Å) distances and Co–Co separation (2.433(1) Å). Electrochemical examination of the resulting tricobalt nitride reveals the material exhibits five accessible redox events. The primary reduction [Co<sub>3</sub>(N)]<sup>0/-</sup> occurs at -1.4 V vs. [Cp<sub>2</sub>Fe]<sup>0/+</sup>. Reaction of the anionic nitride does indeed react with CO<sub>2</sub> to produce 0.5 eq. oxalate and the oxidized nitride (Figure 4). Given this is the first complex that reduces CO<sub>2</sub> via an *inner-sphere mechanism* well below the one-electron reduction potential of CO<sub>2</sub>, we are actively investigating the nature of how the cluster mechanistically activates the substrate and the potential for Co<sub>3</sub>(μ<sup>3</sup>-E) (E = N, C, S, O) complexes to function as viable electroreduction catalysts.



**Scheme 3.** Synthesis of anionic tricobalt nitrido complex and its reactivity with CO<sub>2</sub> to afford oxalate and the neutral nitride product.

(SA 3 – *Dinucleating ligand platforms*) Using the catalysts prepared, catalyst efficacy has been determined via substrate uptake and electrocatalytic experiments. Stoichiometric reactions between the bimetallic units and CO<sub>2</sub> have elucidated that substrate binding occurs as proposed; however, bifunctional perturbations have not lowered the overall barrier to primary nucleophile reduction. Electrocatalytic competency has been assessed as a function of H<sub>2</sub>O and CO production as a function of total current passed to the cathode. The electrocatalytic CO<sub>2</sub> reduction from all three species ((L)Co, (L-OH)Co, and (L-NH)Co) were surveyed under the following conditions: CO<sub>2</sub>-saturated DMF, NaClO<sub>4</sub>, glassy-C working electrode. A representative experiment using varying concentrations of *p*-toluenesulfonic acid (0.1→0.5mM acid; 0.2mM

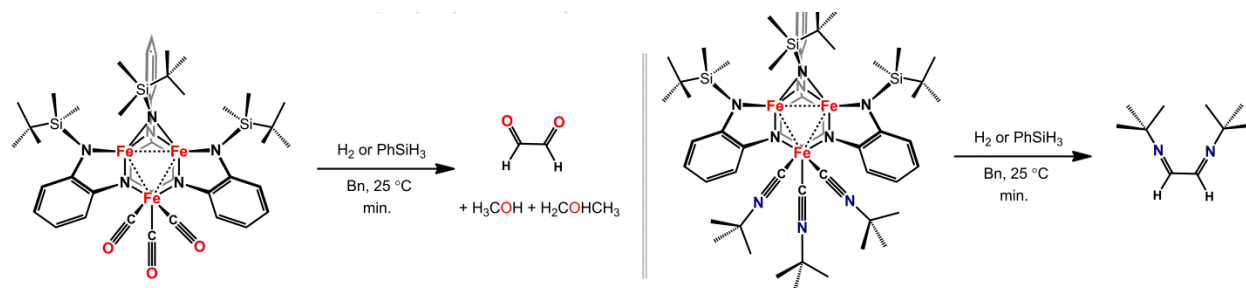
catalyst) is shown in Figure 4. The precatalysts ((L)Co, (L-OH)Co, and (L-NH)Co) all display modest activity for the catalytic reduction of CO<sub>2</sub>, the most active of which is the (L-OH)Co complex. Each of the catalyst precursors display the onset of catalytic current from -2.2 to -2.5V, well in excess of the single-electron, outer-sphere reduction of CO<sub>2</sub> to its radical anion (CO<sub>2</sub><sup>•-</sup>). The background reaction of *p*-toluenesulfonic acid and CO<sub>2</sub> in the absence of catalyst does show the onset of catalytic reduction of the acid (*E*<sub>pc</sub>: -2.4 V, *I*<sub>pc</sub>: -15 μA), but the current wave is less by greater than an order of magnitude from when catalyst is present (*E*<sub>pc</sub>: -2.3 V, *I*<sub>pc</sub>: -110 μA). Furthermore, reduction of the *p*-toluenesulfonic acid does not produce CO gas in the absence of catalyst, where head space analysis of the electrochemical cell shows the build-up of CO gas by IR. The background reactivity for any of the catalysts for proton reduction was surveyed with the analogous electrochemical conditions in the absence of CO<sub>2</sub>. Although a small catalytic wave is observed with increasing acid concentrations, the peak current values (*E*<sub>pc</sub>: -2.4 V, *I*<sub>pc</sub>: -25 to -40 μA) are similar to the background reaction (i.e., no Co catalyst). Examination of the headspace to determine the chemoselectivity for CO<sub>2</sub> reduction vs. proton reduction showed a significant amount of H<sub>2</sub> evolution by GC-MS analysis, even with saturated CO<sub>2</sub> solutions. We determined that with the large overpotentials required to achieve electron transfer to CO<sub>2</sub>, proton reduction could not be avoided. While the productive reduction of CO<sub>2</sub> is promising, the potential to achieve the reduction is very low. As seen from the stoichiometric reductions of (L)Co and (L-OH)Co, the primary locus of reduction is often the imine functionality for the former and the ligand imine *and* hydroxy groups in the latter. In the stoichiometric reductions of CO<sub>2</sub>, K metal was used as the reductant. In the electrochemical reduction, Na<sup>+</sup> ions likely occupy the bis-hydroxy pocket. It is uncertain if the hydroxy groups remain protonated under the acidic conditions.



**Figure 4.** Cyclic voltammograms of 2.0 mM solutions in DMF saturated with CO<sub>2</sub> of (L-OH)Co and varying concentrations of *p*-toluenesulfonic acid (red 0.1 mM, green 0.2 mM, yellow, 0.3 mM, purple 0.4 mM) referenced to Fc/Fc<sup>+</sup> (0.1M NaClO<sub>4</sub>, scan rate = 50mV/min, working electrode: glassy C, counter: Pt wire, reference: Ag wire). Inset shows control experiment of cyclic voltammogram of *p*-toluenesulfonic acid at the same concentrations with saturated CO<sub>2</sub> solutions in DMF.



(SA 4 – *Dipyrin platforms for CO reductive coupling*) We have targeted reductive CO coupling utilizing Fe-based dipyrromethene platforms developed in our labs. We have generated a family of three- and four-coordinate ferrous alkyl complexes featuring the dipyrin ligand and an ancillary alkyl or aryl ligand afforded by metathesis from the ferrous chloride precursor and the appropriate Grignard or alkyl-lithium reagent. Preliminary screening of these complexes show diminished activity for direct CO insertion into the metal-alkyl bond under standard reaction conditions. The weak-field property of the dipyrin ligands gives rise to high-spin complexes, even with strong-field ligands (e.g., imidos, alkyls).<sup>11,12</sup> As a result, the materials are not optimized to bind and activate  $\pi$ -acidic ligands like CO. Surprisingly, the reduced Fe<sup>I</sup> complex does not bind CO to an appreciable extent (labile under vacuum), which suggests reductive coupling of CO on these platforms is not likely.



**Scheme 4.** Reductive coupling of CO and isonitriles via addition of silane or H<sub>2</sub> to cluster complexes.

(SA – Cluster mediated CO reductive coupling) Reaction of isolated (t<sup>bs</sup>L)Fe<sub>3</sub>(CO)<sub>3</sub> (afforded by addition of CO to all ferrous precursor) with excess hydrogen gas (1 atm) or PhSiH<sub>3</sub> effects an immediate reaction (Scheme 4). The tricarbonyl is rapidly consumed and GC-MS analysis reveals several C–C coupled products (oxalaldehyde, methanol, and ethanol). The reaction with the *tert*-butylisocyanide analogue also displays reductive coupling upon exposure to PhSiH<sub>3</sub> or hydrogen, but the only organic product identified thus far is the diimine. The secondary reaction with the hydrogen carrier must be facilitated by the diiron moiety, given the Fe(CE)<sub>3</sub> (E = O, N<sup>t</sup>Bu) ion is low-spin and electronically saturated. Overall, the (t<sup>bs</sup>L)Fe<sub>3</sub> unit provides a bifunctional platform for binding the small molecule substrate and subsequent reduction and can be viewed as a single molecule functional analogue to heterogeneous Fischer-Tropsch<sup>13</sup> catalysts. This reactivity must also be compared with mononuclear early transition metal ligands that require very strong chemical reductants to induce the reductive coupling of these ligands,<sup>14</sup> which highlights the utility of the polynuclear approach. Given the extremely mild conditions under which this reaction takes place, we will investigate the scope of this reaction to include other substrates and determine the integrity of the molecular unit that is facilitating the reaction.

### C. Significance

A significant challenge facing long-duration or high altitude air travel is the transportation of the fuel itself. Our targeted strategy is to transform CO<sub>2</sub> into viable building blocks for synthetic fuels through the development of a new class of chemical catalysts. Coupled with existing solar energy harvesting technology, the catalysts developed herein will provide one of the key components for advanced energy storage and mobile energy generation. The research

proposed here addresses a fundamental stumbling block to the electrocatalytic transformation of CO<sub>2</sub> to fuel—the large barrier associated with C–O bond cleavage. Progress on this front is essential to enabling direct electrocatalytic production of fuel containing C–C bonds. On a shorter timeframe, this research targets catalysts that produce two C1 products of great utility: CO, the C component of *syngas*, from which all fuels can be prepared.

#### D. Conclusions

The goal of this research is to synthesize rigid ligand platforms to support the cooperative, bifunctional activation of CO<sub>2</sub> as a substrate. To this end, easily modified bifunctional ligand scaffolds are proposed to include both nucleophilic and electrophilic metal sites to facilitate both CO and O-atom capture, respectively, in a CO<sub>2</sub> activation event. Our hypothesis derives from careful scrutinizing of the known biological and synthetic CO<sub>2</sub> activating systems. The ultimate utility of these systems will be measured by their ability to catalyze the conversion of CO<sub>2</sub> into CO and water, providing a much needed sink for CO<sub>2</sub> and a valuable C1 resource for Fischer-Tropsch synthesis.

Using easily tailored *salen* and *salan* ligand platforms, we have observed facile CO<sub>2</sub> uptake and activation utilizing a family of Co<sup>I</sup> coordination complexes. The extent to which the CO<sub>2</sub> substrate was activated was a function of the ligand architecture and coordination complex composition. While the parent *salen* platform exhibits modest CO<sub>2</sub> activation (as judged by IR spectroscopy), the *salan* and *salen* platform featuring hydroxide functionalities in the secondary coordination sphere (**L-OH**) facilitate greater CO<sub>2</sub> substrate activation. This results from amine or hydroxide deprotonation and multiple K<sup>+</sup> ions in the immediate coordination sphere, contributing to the binding, stabilization, and activation of the CO<sub>2</sub> substrate. The mechanism of complex reduction involves primary reduction of the ligand imine functionality, followed by electron-transfer to the metal center upon introduction of CO<sub>2</sub> substrate. The family of Co-coordination complexes were shown to exhibit electrocatalytic reduction of CO<sub>2</sub> in the presence of a mild acid (or organic nucleophile) to produce CO gas and H<sub>2</sub>O. A new electrophilic Fe-based complex was discovered to reductively couple CO gas under very mild conditions, demonstrating the primary step of higher paraffin synthesis from CO.

Despite the early successes demonstrating the viability of our original bifunctional platforms to reduce CO<sub>2</sub> under electrocatalytic conditions, a key liability of our design was quickly exposed: we did not have an easy handle to alter the reduction potential to Co<sup>I</sup> within the *salen*/*salan* platforms. This resulted in very negative potentials being required to achieve the active state of the metal (when CO<sub>2</sub> binds), regardless of the secondary coordination sphere perturbations. Thus, the key design element (the central metal binding site) could not achieve a mild route for CO<sub>2</sub> activation. Unsurprisingly, the onset of catalysis for several of the platforms investigated operated at potentials suggestive of outer-sphere electron transfer to substrate, suggesting the primary metal reductant and its secondary coordination sphere have little active role in reducing CO<sub>2</sub>. These negative findings spurred our interest in developing alternative strategies to discover new routes towards CO<sub>2</sub> and CO reduction chemistry.

Both metal-dipyrin and cluster complexes were investigated as platforms to observe substrate reduction chemistry. While the dipyrin systems demonstrated a high-degree of tunability to manipulate the bound transition metal redox potentials, the resultant complexes required strong chemical reductants to access complexes capable of engaging CO<sub>2</sub> or CO. Furthermore, the CO reductive coupling chemistry discovered on related tris-pyrrolide ligand systems did not transfer to the weak-field dipyrin ligand sets. Indeed, the weak-field

environment engendered by these ligand sets was evidenced by the lack of ferrous alkyl and aryl complexes to insert or react with CO.

The most promising avenue worthy of further investigation centers on the clusters developed in the last year of this funding cycle. The clusters exhibit cathodically shifted redox potentials for clusters featuring metals in their standard M<sup>II</sup> redox states. The presence of multiple metals in the reaction site contributes to the cathodic shifting. Two significant reactions were discovered: (1) a reactive Co<sub>3</sub>(N) complex is capable of reducing CO<sub>2</sub> well below the one-electron reduction potential for CO<sub>2</sub>, suggesting the CO<sub>2</sub> engages the cluster in an inner-sphere mechanism; (2) reductive coupling of CO and CNR ligands was observed at Fe<sub>3</sub>(CO/CNR)<sub>3</sub> clusters upon exposure to hydrogen gas or upon reaction with phenylsilane as a reductant. For the CO<sub>2</sub> reduction, further reaction sites could be envisioned where the light atom bridge or the cluster metal components can be altered to reduce the barrier to CO<sub>2</sub> reduction further. The same design strategies can be envisioned to enhance the reductive coupling of CO and CNR. The viability of these as-synthesized clusters as electrocatalysts has yet to be demonstrated, but studies to determine their efficacy are currently underway.

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